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Publication Office
American Public Health Association
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4500-SO_4^{2-} SULFATE*

4500-SO_4^{2-} A. Introduction

1. Occurrence

Sulfate (SO_4^{2-}) is widely distributed in nature and may be present in natural waters in concentrations ranging from a few to several thousand milligrams per liter. Mine drainage wastes may contribute large amounts of SO_4^{2-} through pyrite oxidation. Sodium and magnesium sulfate exert a cathartic action.

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* Approved by Standard Methods Committee, 1990.

2. Selection of Method

The ion chromatographic method (B) is suitable for sulfate concentrations above 0.1 mg/L. The gravimetric methods (C and D) are suitable for SO_4^{2-} concentrations above 10 mg/L; use one of these methods for accurate results. The turbidimetric method (E) is applicable in the range of 1 to 40 mg SO_4^{2-}/L. The automated methylthymol blue method (F) is the procedure for analyzing large numbers of samples for sulfate alone when the equipment is available; about 30 samples can be analyzed per hour.

3. Sampling and Storage

In the presence of organic matter certain bacteria may reduce SO_4^{2-} to S^{2-}. To avoid this, store heavily polluted or contaminated samples at 4°C.

4500-SO_4^{2-} B. Ion Chromatographic Method

See Section 4110.

4500-SO_4^{2-} C. Gravimetric Method with Ignition of Residue

1. General Discussion

a. Principle: Sulfate is precipitated in a hydrochloric acid (HCl) solution as barium sulfate ($BaSO_4$) by the addition of barium chloride ($BaCl_2$).

The precipitation is carried out near the boiling temperature, and after a period of digestion the precipitate is filtered, washed with water until free of Cl^-, ignited or dried, and weighed as $BaSO_4$.

b. Interference: The gravimetric determination of SO_4^{2-} is subject to many errors, both positive and negative. In potable waters where the mineral concentration is low, these may be of minor importance.

1) Interferences leading to high results—Suspended matter, silica, $BaCl_2$ precipitant, NO_3^-, SO_3^{2-} and occluded mother liquor in the precipitate are the principal factors in positive errors. Suspended matter may be present in both the sample and the precipitating solution; soluble silicate may be rendered insoluble and SO_3^{2-} may be oxidized to SO_4^{2-} during analysis. Barium nitrate [$Ba(NO_3)_2$], $BaCl_2$, and water are occluded to some extent with the $BaSO_4$ although water is driven off if the temperature of ignition is sufficiently high.

2) Interferences leading to low results—Alkali metal sulfates frequently yield low results. This is true especially of alkali hydrogen sulfates. Occlusion of alkali sulfate with $BaSO_4$ causes substitution of an element of lower atomic weight than barium in the precipitate. Hydrogen sulfates of alkali metals act similarly and, in addition, decompose on being heated. Heavy metals, such as chromium and iron, cause low results by interfering with the complete precipitation of SO_4^{2-} and by formation of heavy metal sulfates. $BaSO_4$ has small but significant solubility, which is increased in the presence of acid. Although an acid medium is necessary to prevent precipitation of barium carbonate and phosphate, it is important to limit its concentration to minimize the solution effect.

2. Apparatus

a. Steam bath.

b. Drying oven, equipped with thermostatic control.

c. Muffle furnace, with temperature indicator.

d. Desiccator.

e. Analytical balance, capable of weighing to 0.1 mg.

f. Filter: Use one of the following:

1) *Filter paper,* acid-washed, ashless hard-finish, sufficiently retentive for fine precipitates.

2) *Membrane filter,* with a pore size of about 0.45 μm.

g. Filtering apparatus, appropriate to the type of filter selected. (Coat membrane filter holder with silicone fluid to prevent precipitate from adhering.)

3. Reagents

a. Methyl red indicator solution: Dissolve 100 mg methyl red sodium salt in distilled water and dilute to 100 mL.

b. Hydrochloric acid, HCl, 1 + 1.

c. Barium chloride solution: Dissolve 100 g $BaCl_2 \cdot 2H_2O$ in 1 L distilled water. Filter through a membrane filter or hard- finish filter paper before use; 1 mL is capable of precipitating approximately 40 mg SO_4^{2-}.

d. Silver nitrate-nitric acid reagent: Dissolve 8.5 g $AgNO_3$ and 0.5 mL conc HNO_3 in 500 mL distilled water.

*e. Silicone fluid.**

4. Procedure

a. Removal of silica: If the silica concentration exceeds 25 mg/L, evaporate sample nearly to dryness in a platinum dish on a steam bath. Add 1 mL HCl, tilt, and rotate dish until the acid comes in complete contact with the residue. Continue evaporation to dryness. Complete drying in an oven at 180°C and if organic matter is present, char over flame of a burner. Moisten residue with 2 mL distilled water and 1 mL HCl, and evaporate to dryness on a steam bath. Add 2 mL HCl, take up soluble residue in hot water, and filter. Wash insoluble silica with several small portions of hot distilled water. Combine filtrate and washings. Discard residue.

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* "Desicote" (Beckman), or equivalent.

b. Precipitation of barium sulfate: Adjust volume of clarified sample to contain approximately 50 mg SO_4^{2-} in a 250-mL volume. Lower concentrations of SO_4^{2-} may be tolerated if it is impracticable to concentrate sample to the optimum level, but in such cases limit total volume to 150 mL. Adjust pH with HCl to pH 4.5 to 5.0, using a pH meter or the orange color of methyl red indicator. Add 1 to 2 mL HCl. Heat to boiling and, while stirring gently, slowly add warm $BaCl_2$ solution until precipitation appears to be complete; then add about 2 mL in excess. If amount of precipitate is small, add a total of 5 mL $BaCl_2$ solution. Digest precipitate at 80 to 90°C, preferably overnight but for not less than 2 h.

c. Filtration and weighing: Mix a small amount of ashless filter paper pulp with the $BaSO_4$, quantitatively transfer to a filter, and filter at room temperature. The pulp aids filtration and reduces the tendency of the precipitate to creep. Wash precipitate with small portions of warm distilled water until washings are free of Cl^- as indicated by testing with $AgNO_3$-HNO_3 reagent. Place filter and precipitate in a weighed platinum crucible and ignite at 800°C for 1 h. Do not let filter paper flame. Cool in desiccator and weigh.

5. Calculation

$$\text{mg } SO_4^{2-}/L = \frac{\text{mg } BaSO_4 \times 411.6}{\text{mL sample}}$$

6. Precision and Bias

A synthetic sample containing 259 mg SO_4^{2-}/L, 108 mg Ca^{2+}/L, 82 mg Mg^{2+}/L, 3.1 mg K^+/L, 19.9 mg Na^+/L, 241 mg Cl^-/L, 0.250 mg NO_2^--N/L, 1.1 mg NO_3^--N/L, and 42.5 mg total alkalinity/L (contributed by $NaHCO_3$) was analyzed in 32 laboratories by the gravimetric method, with a relative standard deviation of 4.7% and a relative error of 1.9%.

7. Bibliography

HILLEBRAND, W.F. et al. 1953. Applied Inorganic Analysis, 2nd ed. John Wiley & Sons, New York, N.Y.

KOLTHOFF, I.M., E.J. MEEHAN, E.B. SANDELL & S. BRUCKENSTEIN. 1969. Quantitative Chemical Analysis, 4th ed. Macmillan Co., New York, N.Y.

4500-SO_4^{2-} D. Gravimetric Method with Drying of Residue

1. General Discussion

See Method C, preceding.

2. Apparatus

With the exception of the filter paper, all of the apparatus cited in Section 4500-SO_4^{2-}.C.2 is required, plus the following:

a. Filters: Use one of the following:

1) *Fritted-glass filter,* fine ("F") porosity, with a maximum pore size of 5 µm.

2) *Membrane filter,* with a pore size of about 0.45 µm.

b. Vacuum oven.

3. Reagents

All the reagents listed in Section 4500-SO_4^{2-}.C.3 are required.

4. Procedure

a. Removal of interference: See Section 4500-SO_4^{2-}.C.4*a*.

b. Precipitation of barium sulfate: See Section 4500-SO_4^{2-}.C.4*b*.

c. Preparation of filters:

1) Fritted glass filter—Dry to constant weight in an oven maintained at 105°C or higher, cool in desiccator, and weigh.

2) Membrane filter—Place filter on a piece of filter paper or a watch glass and dry to constant weight* in a vacuum oven at 80°C, while maintaining a vacuum of at least 85 kPa or in a conventional oven at a temperature of 103 to 105°C. Cool in desiccator and weigh membrane only.

d. Filtration and weighing: Filter $BaSO_4$ at room temperature. Wash precipitate with several small portions of warm distilled water until washings are free of Cl^-, as indicated by testing with $AgNO_3$-HNO_3 reagent. If a membrane filter is used add a few drops of silicone fluid to the suspension before filtering, to prevent adherence of precipitate to holder. Dry filter and precipitate by the same procedure used in preparing filter. Cool in a desiccator and weigh.

5. Calculation

$$\text{mg } SO_4^{2-}/L = \frac{\text{mg } BaSO_4 \times 411.6}{\text{mL sample}}$$

6. Bibliography

See Section 4500-SO_4^{2-}.C.7.

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* Constant weight is defined as a change of not more than 0.5 mg in two successive operations consisting of heating, cooling in desiccator, and weighing.

4500-SO_4^{2-} E. Turbidimetric Method

1. General Discussion

a. Principle: Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

b. Interference: Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. If both are small in comparison with the SO_4^{2-} concentration, correct for interference as indicated in ¶ 4*d* below. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate $BaSO_4$ satisfactorily.

In potable waters there are no ions other than SO_4^{2-} that will form insoluble compounds with barium under strongly acid conditions. Make determination at room temperature; variation over a range of 10°C will not cause appreciable error.

c. Minimum detectable concentration: Approximately 1 mg SO_4^{2-}/L.

2. Apparatus

a. Magnetic stirrer: Use a constant stirring speed. It is convenient to incorporate a fixed resistance in series with the motor operating the magnetic stirrer to regulate stirring speed. Use magnets of identical shape and size. The exact speed of stirring is not critical, but keep it constant for each run of samples and standards and adjust it to prevent splashing.

b. Photometer: One of the following is required, with preference in the order given:

1) *Nephelometer.*

2) *Spectrophotometer,* for use at 420 nm, providing a light path of 2.5 to 10 cm.

3) *Filter photometer,* equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 2.5 to 10 cm.

c. Stopwatch or electric timer.

d. Measuring spoon, capacity 0.2 to 0.3 mL.

3. Reagents

a. Buffer solution A: Dissolve 30 g magnesium chloride, $MgCl_2 \cdot 6H_2O$, 5 g sodium acetate, $CH_3COONa \cdot 3H_2O$, 1.0 g potassium nitrate, KNO_3, and 20 mL acetic acid, CH_3COOH (99%), in 500 mL distilled water and make up to 1000 mL.

b. Buffer solution B (required when the sample SO_4^{2-} concentration is less than 10 mg/L): Dissolve 30 g $MgCl_2 \cdot 6H_2O$, 5 g $CH_3COONa \cdot 3H_2O$, 1.0 g KNO_3, 0.111 g sodium sulfate, Na_2SO_4, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

c. Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh. In standardization, uniform turbidity is produced with this mesh range and the appropriate buffer.

d. Standard sulfate solution: Prepare a standard sulfate solution as described in 1) or 2) below; 1.00 mL = 100 μg SO_4^{2-}.

1) Dilute 10.4 mL standard 0.0200*N* H_2SO_4 titrant specified in Alkalinity, Section 2320B.3*c*, to 100 mL with distilled water.

2) Dissolve 0.1479 g anhydrous Na_2SO_4 in distilled water and dilute to 1000 mL.

4. Procedure

a. Formation of barium sulfate turbidity: Measure 100 mL sample, or a suitable portion made up to 100 mL, into a 250-mL erlenmeyer flask. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 60 ± 2 s at constant speed.

b. Measurement of barium sulfate turbidity: After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5 ± 0.5 min.

c. Preparation of calibration curve: Estimate SO_4^{2-} concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying SO_4^{2-} standards through the entire procedure. Space standards at 5-mg/L increments in the 0- to 40-mg/L SO_4^{2-} range. Above 40 mg/L accuracy decreases and $BaSO_4$ suspensions lose stability. Check reliability of calibration curve by running a standard with every three or four samples.

d. Correction for sample color and turbidity: Correct for sample color and turbidity by running blanks to which $BaCl_2$ is not added.

5. Calculation

$$\text{mg } SO_4^{2-}/\text{L} = \frac{\text{mg } SO_4^{2-} \times 1000}{\text{mL sample}}$$

If buffer solution A was used, determine SO_4^{2-} concentration directly from the calibration curve after subtracting sample absorbance before adding $BaCl_2$. If buffer solution B was used subtract SO_4^{2-} concentration of blank from apparent SO_4^{2-} concentration as determined above; because the calibration curve is not a straight line, this is not equivalent to subtracting blank absorbance from sample absorbance.

6. Precision and Bias

With a turbidimeter,[*] in a single laboratory with a sample having a mean of 7.45 mg SO_4^{2-}/L, a standard deviation of 0.13 mg/L and a coefficient of variation of 1.7% were obtained. Two samples dosed with sulfate gave recoveries of 85 and 91%.

7. Bibliography

SHEEN, R.T., H.L. KAHLER & E.M. ROSS. 1935. Turbidimetric determination of sulfate in water. *Ind. Eng. Chem.*, Anal. Ed. 7:262.

THOMAS, J.F. & J.E. COTTON. 1954. A turbidimetric sulfate determination. *Water Sewage Works* 101:462.

ROSSUM, J.R. & P. VILLARRUZ. 1961. Suggested methods for turbidimetric determination of sulfate in water. *J. Amer. Water Works Assoc.* 53:873.

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[*] Hach 2100 A.

4500-SO_4^{2-} F. Automated Methylthymol Blue Method

1. General Discussion

a. Principle: Barium sulfate is formed by the reaction of the SO_4^{2-} with barium chloride ($BaCl_2$) at a low pH. At high pH excess barium reacts with methylthymol blue to produce a blue chelate. The uncomplexed methylthymol blue is gray. The amount of gray uncomplexed methylthymol blue indicates the concentration of SO_4^{2-}.

b. Interferences: Because many cations interfere, use an ion-exchange column to remove interferences.

Molybdenum, often used to treat cooling waters, has been shown to cause a strong positive bias with this method, even with as little as 1 mg Mo/L.

c. Application: This method is applicable to potable, surface, and saline waters as well as domestic and industrial wastewaters over a range from about 10 to 300 mg SO_4^{2-}/L.

2. Apparatus

a. Automated analytical equipment: The required continuous-flow analytical instrument* consists of the interchangeable components shown in Figure 4500-SO_4^{2-}:1.

b. Ion-exchange column: Fill a piece of 2-mm-ID glass tubing about 20 cm long with the ion-exchange resin.† To simplify filling column put resin in distilled water and aspirate it into the tubing, which contains a glass-wool plug. After filling, plug other end of tube with glass wool. Avoid trapped air in the column.

3. Reagents

a. Barium chloride solution: Dissolve 1.526 g $BaCl_2 \cdot 2H_2O$ in 500 mL distilled water and dilute to 1 L. Store in a polyethylene bottle.

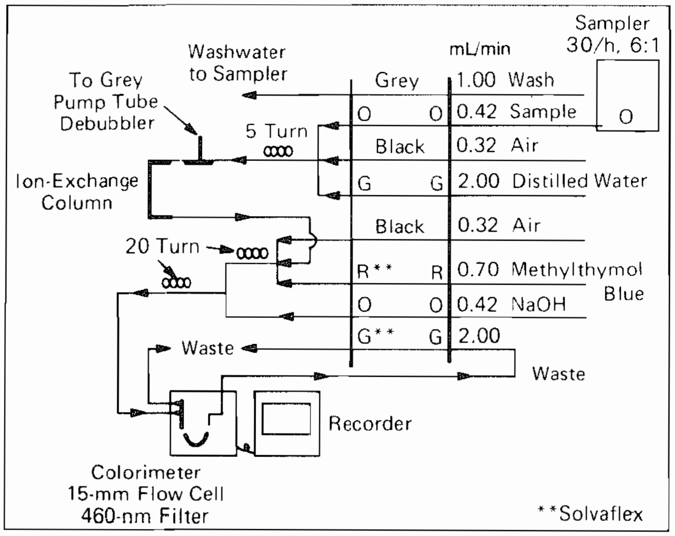

Figure 4500-SO_4^{2-}:1. Sulfate manifold.

b. Methylthymol blue reagent: Dissolve 118.2 mg methylthymol blue‡ in 25 mL $BaCl_2$ solution. Add 4 mL 1*N* HCl and 71 mL distilled water and dilute to 500 mL with 95% ethanol. Store in a brown glass bottle. Prepare fresh daily.

c. Buffer solution, pH 10.1: Dissolve 6.75 g NH_4Cl in 500 mL distilled water. Add 57 mL conc NH_4OH and dilute to 1 L with distilled water. Adjust pH to 10.1 and store in a polyethylene bottle. Prepare fresh monthly.

d. EDTA reagent: Dissolve 40 g tetrasodium ethylenediaminetetraacetate in 500 mL pH 10.1 buffer solution. Dilute to 1 L with pH 10.1 buffer solution and store in a polyethylene bottle.

e. Sodium hydroxide solution, 0.36*N:* Dissolve 7.2 g NaOH in 500 mL distilled water. Cool and make up to 1 L with distilled water.

f. Stock sulfate solution: Dissolve 1.479 g anhydrous Na_2SO_4 in 500 mL distilled water and dilute to 1000 mL; 1.00 mL = 1.00 mg SO_4^{2-}.

g. Standard sulfate solutions: Prepare in appropriate concentrations from 10 to 300 mg SO_4^{2-}/L, using the stock sulfate solution.

4. Procedure

Set up the manifold as shown in Figure 4500-SO_4^{2-}:1 and follow the general procedure described by the manufacturer.

After use, rinse methylthymol blue and NaOH reagent lines in water for a few minutes, rinse them in the EDTA solution for 10 min, and then rinse in distilled water.

5. Calculation

Prepare standard curves by plotting peak heights of standards processed through the manifold against SO_4^{2-} concentrations in standards. Compute sample SO_4^{2-} concentration by comparing sample peak height with standard curve.

6. Precision and Bias

With a Technicon Autoanalyzer II in a single laboratory a sample with an average concentration of about 28 mg SO_4^{2-}/L had a standard deviation of 0.68 mg/L and a coefficient of variation of 2.4%. In two samples with added SO_4^{2-}, recoveries were 91% and 100%.

7. Bibliography

LAZRUS, A.L., K.C. HILL & J.P. LODGE. 1965. A new colorimetric microdetermination of sulfate ion. *In* Automation in Analytical Chemistry. Technicon Symposium.

COLOROS, E., M. R. PANESAR & F.P. PERRY. 1976. Linearizing the calibration curve in determination of sulfate by the methylthymol blue method. *Anal. Chem.* 48:1693.

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* Technicon™ Autoanalyzer™ or equivalent.

† Ion-exchange resin Bio-Rex 70, 20-50 mesh, sodium form, available from Bio-Rad Laboratories, Richmond, Calif. 94804, or equivalent.

‡ Eastman Organic Chemicals, Rochester, N.Y. 14615, No. 8068 3′.3″ bis [*N,N*-bis(carboxymethyl)-aminolmethyl] thymolsulfonphthalein pentasodium salt.